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Effects of microstructure on microwave dielectric properties of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions

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Abstract

The effect of the variations in the microstructure and lattice parameters on the microwave dielectric properties of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions with and without MgO were evaluated in this study. The unit cell volumes with MgO are non-linearly changed with increasing the composition x, whereas those without MgO are parabolically increased. Thus, Mg^{2+} ions are substituted for Cu of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions at $x=0$ and 0.25, and then Mg^{2+} substitution for Zn is induced over the composition $x=0.5$. In this case, the variations in the microstructure with substitution influence the $Q{\cdot}f$ values, and the highest value is 128333 GHz at $x=0.25$. The highest value of $Q{\cdot}f$ without MgO, is 113969 GHz at $x=1$. It is recognized that the grain growth induced by the difference of the sintering time exerts on $Q{\cdot}f$ values.

Keywords: Dielectric properties; MgO; Powder: solid state reaction; X-ray method

1. Introduction

The Y_2BaCuO_5 compound is known to be an insulator phase that is produced when the high-Tc superconductor $YBa_2Cu_3O_{7-x}$ ceramics are prepared. The crystal structure of Y_2BaCuO_5 was refined by Michel and Revue[1] and it had an orthorhombic structure with Y_2O_{11} and BaO_{11} polyhedra, and CuO_5 pyramid.

Microwave dielectric properties of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions were reported,[2] and it was found that $Q{\cdot}f$ values were extremely improved when Cu was substituted by Zn. However, the influences of the microstructure and crystal structure with Zn substitution for Cu on these properties have not yet been evaluated. For this reason, the effects of the microstructure and crystal structure on the microwave dielectric properties are investigated by means of FE–SEM and Rietveld analysis, respectively. Moreover, in order to obtain higher $Q{\cdot}f$ values and an appropriate τ_f close to 0 ppm/°C, 5 wt.% MgO was doped into $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions as a sintering aid, and the resulting microstructures were also studied in this work.

2. Experimental

$Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions were synthesized by means of the conventional solid-state reaction method, using Y_2O_3, $BaCO_3$, CuO and ZnO powders of 99.9% purity. Weights of these powders were stoichiometrically determined with the composition of x ranging from 0 to 1 and mixed with acetone. Then, these were calcined in an alumina crucible at 950°C for 20 h in air. The calcined powders with and without 5 wt.% MgO were pressed into pellets 12 mm in diameter and 7 mm thick under a pressure of 100 MPa after crushing and grinding with an organic binder, passing through a screen mesh. The sintering temperatures were determined by differential thermal analysis (DTA) and thermogravimetry (TG), and then these pellets were sintered at respective temperatures for 2 and 10 h in air. Subsequently, the sintered pellets were polished and annealed at 800°C to remove any strain. The phases of the synthesized materials were identified by X-ray powder diffraction (XRPD), using CuK_α filtered through Ni foil. The lattice parameters of the solid solutions with substituted Zn for Cu are clarified at room temperature by using the Rietveld analysis[3] program "RIETAN".[4] The microwave dielectric properties of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions with and without MgO were measured

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according to Hakki and Coleman's method.[5] In addition, the microstructure of the solid solutions was investigated by using FE–SEM and energy dispersive X-ray analysis (EDX).

3. Results and discussion

From the XRPD profiles, it can be observed that $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions are formed in a single phase over the whole composition range, with and without MgO sintered for 2 and 10 h. Moreover, $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions and MgO were identified in the XRPD patterns of the samples with MgO and then the existence of the impurity phase was not recognized. Table 1 shows the lattice parameters and reliability factors of the Rietveld analysis for the solid solutions with and without 5 wt.% MgO sintered for 10 h, and then Fig. 1 shows the unit cell volumes of these samples sintered for 10 h with and without MgO. Concerning the variations in the lattice parameters of the solid solutions without MgO, the lattice parameters, a and b, are almost linearly increased, whereas the lattice parameter c is decreased with increasing the composition x, as shown in Table 1. Also, the significant variations in the lattice parameters between the solid solutions sintered at 2 and 10 h have not been recognized in this study. Thus, the variations in these parameters as mentioned above are attributed to the differences of the ionic radii between Cu^{2+} and Zn^{2+} ions located at the bottom of the MO_5 (M = Cu and/or Zn) pyramid.

Comparing the lattice parameters of the solid solutions with and without MgO, the lattice parameters of those with MgO at $x=0$ and 0.25 are larger than those without MgO. On the other hand, the lattice parameters with MgO ranging from 0.5 to 1 are smaller than those without MgO, as listed in Table 1. According to the ionic radii reported by Shannon,[6] the ionic radii of Cu^{2+}, Mg^{2+} and Zn^{2+} ions are 0.65, 0.66 and 0.68 Å, respectively, because the coordination number is five. Therefore, the increments and decrements of the lattice parameters at $x=0$ and 1 with and without MgO are considered to be caused by Mg substitution for Cu and Zn, respectively. As for the variations in the lattice parameters at $x=0.25$ and 0.75, these are induced by the preferential Mg substitution for M depending on the composition x, i.e. partially substituted Cu by Mg at $x=0.25$ and then the Zn substitutions for Mg at $x=0.75$, resulting in the variations of the lattice parameters with and without MgO as shown in Table 1. In addition, the lattice parameters with MgO at $x=0.5$ are decreased in comparison with those obtained at $x=0.75$

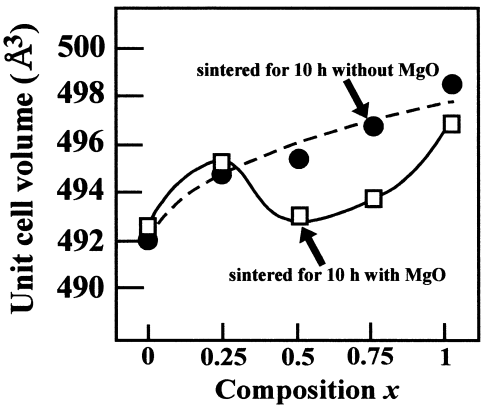

Fig. 1. Unit cell volumes of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions with and without MgO as a function of composition x.

Table 1
Lattice parameters and the reliability factors of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions with and without MgO sintered for 10 h

Composition x	$x=0$	$x=0.25$	$x=0.5$	$x=0.75$	$x=1$
Sintering time (h)	10	10	10	10	10
Lattice parameter a (Å)	12.1866(5)	12.2589(9)	12.2636(5)	12.3000(7)	12.3392(6)
Lattice parameter b (Å)	5.6622(2)	5.6833(4)	5.6860(2)	5.6989(3)	5.7107(2)
Lattice parameter c (Å)	7.1314(2)	7.0973(5)	7.1005(2)	7.0859(4)	7.0727(4)
R_{wp}	7.09	8.47	6.09	12.91	11.81
R_p	4.86	6.42	6.52	9.53	9.10
R_e	3.55	3.94	3.76	3.84	3.93
Composition x	$x=0$ 5 wt.% MgO	$x=0.25$ 5 wt.% MgO	$x=0.5$ 5 wt.% MgO	$x=0.75$ 5 wt.% MgO	$x=1$ 5 wt.% MgO
Sintering time (h)	10	10	10	10	10
Lattice parameter a (Å)	12.1898(5)	12.2658(6)	12.2199(8)	12.2761(9)	12.3328(8)
Lattice parameter b (Å)	5.6638(2)	5.6860(2)	5.6716(3)	5.6856(3)	5.7078(3)
Lattice parameter c (Å)	7.1346(2)	7.1015(3)	7.1151(4)	7.0728(3)	7.0702(4)
R_{wp}	6.58	7.40	8.50	11.81	8.92
R_p	5.24	5.67	6.36	9.10	7.16
R_e	3.43	3.40	3.60	3.93	4.22

and 1. On the basis of the results of the Rietveld analysis, these remarkable decrements are considered to be the effect of Mg substitution for Zn on higher occupancy, comparing with other composition. The crystal structure at $x=0.5$ contains the two CuO_5 and ZnO_5 pyramids with no symmetry in the unit cell. Then, the variation of the atomic distances in these pyramids induces the instability of the crystal structure. Therefore, these decreases of the lattice parameters have been considered to be due to the instability of the crystal structure depending on the composition.

Fig. 2 and Table 2 show the microwave dielectric properties of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions with and without MgO sintered for 2 and 10 h. ε_r of the samples without MgO range from 8.9 to 15.9, and these values increase with increasing the composition x. Therefore, this suggests that these variations in ε_r are closely related to the changes in the lattice parameter of the solid solutions as mentioned above. The slight increase in ε_r between the samples sintered for 2 and 10 h are attributed to the increments of the relative density induced by the difference of the sintering time. The τ_f values of the solid solutions sintered for 2 and 10 h range from −34.5 to −41.9 ppm/°C and −35.0 to −44.5 ppm/°C, respectively, and these values do not depend on variation in the composition. The dependence of τ_f values obtained on the sintering was not recognized in this study. The variations in the crystal structure, i.e. the variations in atomic distances of MO_5 pyramid induced by substituting Zn for Cu, do not influence τ_f because Zn substitution for Cu is not recognized on the improvement of τ_f as listed in Table 2.

Table 2
Dielectric properties of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions with and without MgO

Amount of MgO (wt.%)	Sintering time (h)	x[a]	f[b] (GHz)	ε_r[c]	$Q{\cdot}f$[d] (GHz)	τ_f[e] (ppm/°C)
0	2	0	12.293	8.9	7902	−37.7
0	2	0.25	11.502	12.1	25,639	−34.9
0	2	0.5	10.524	14.1	38,902	−40.1
0	2	0.75	10.533	15.1	41,073	−41.7
0	2	1	10.158	15.7	53,364	−41.9
0	10	0	12.021	9.4	3831	−35.0
0	10	0.25	10.859	14.3	71,141	−38.2
0	10	0.5	10.378	15.1	81,745	−40.1
0	10	0.75	10.297	15.9	108,663	−41.3
0	10	1	10.162	15.4	113,969	−44.5
5	10	0	11.590	10.5	15,523	−45.4
5	10	0.125	11.254	12.8	40,078	−43.3
5	10	0.25	10.503	14.4	128,333	−41.6
5	10	0.5	11.407	10.7	23,699	−39.5
5	10	0.75	11.090	13.0	27,878	−39.0
5	10	1	10.488	15.8	4071	−47.5

[a] x, Composition.
[b] f, Resonant frequency.
[c] ε_r, Dielectric constant.
[d] $Q{\cdot}f$, Quality factor.
[e] τ_f, Temperature coefficient of the resonant frequency.

Both $Q{\cdot}f$ values of the samples sintered for 2 and 10 h increase with the variations in the composition x, and it is recognized that $Q{\cdot}f$ values of the samples without MgO are improved by Zn substitution for Cu. The maximum values are obtained at $x=1$, and the values of the samples sintered for 2 and 10 h are 53364 and 113969 GHz, respectively. In the $Q{\cdot}f$ values of the $x=1$ samples sintered for 10 h, the values are extremely

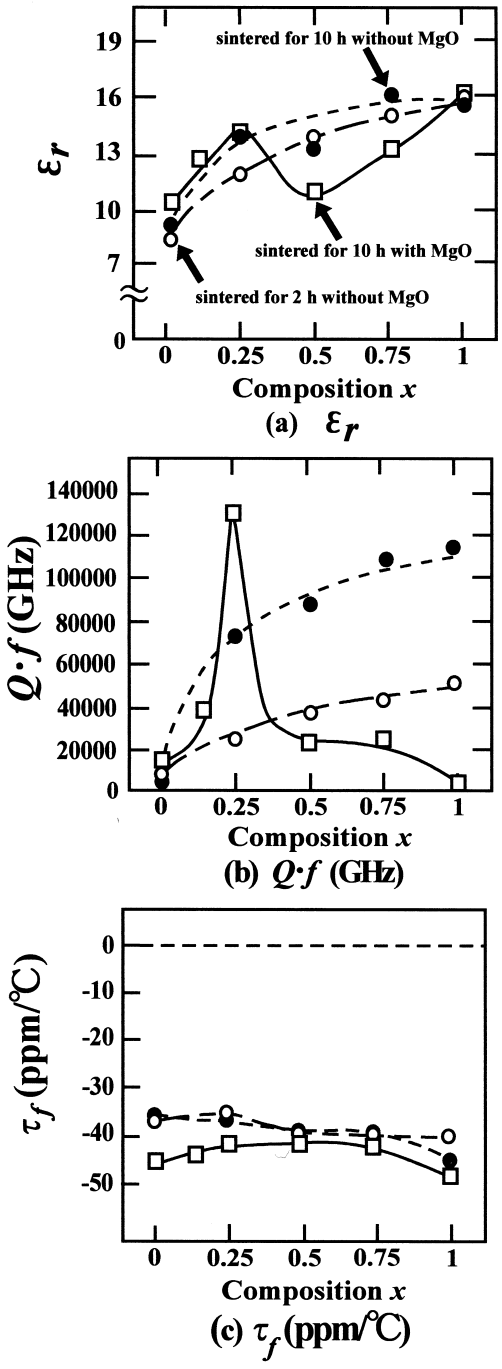

Fig. 2. Microwave dielectric properties of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions with and without MgO as a function of composition x.

improved in comparison with those sintered for 2 h, whereas the differences of $Q{\cdot}f$ values between those sintered for 2 and 10 h at $x=0$ have not been remarkable as shown in Fig. 2. This suggests that the $Q{\cdot}f$ values depend on the sintering time in this system. The microstructures and element distributions of the solid solutions without MgO were observed by means of FE–SEM and EDX analysis in order to evaluate the effects of the microstructure induced by the difference of the sintering time on the microwave dielectric properties. The FE–SEM photographs of the solid solutions for each composition without MgO sintered for 2 and 10 h are shown in Fig. 3. There is increased grain growth with an increase in the composition for both 2 and 10 h. In addition, there is an increase in grain growth of the solid solutions between the samples sintered for 2 h and those sintered for 10 h, although the difference of grain growth at $x=0$ have not been found. The grain size of the solid solutions sintered for 10 h is larger than those sintered for 2 h as shown in Fig. 3. In each of the composition, the impurity phase was not detected from EDX analysis, and these gray-plate like crystals consisted of single phase of the solid solutions were only observed from FE–SEM. Therefore, it is considered that the grain growth of the samples without MgO influences the improvement of $Q{\cdot}f$ values as described above. From the results of FE–SEM and EDX analysis, it is clarified that the grain growth in this system improves the $Q{\cdot}f$ values by increasing in the unit cell volume resulted with Zn substitution for Cu. Moreover, much higher $Q{\cdot}f$ values were obtained by increasing in the sintering time in this study, compared with those sintered for 2 h. Therefore, the grain growth induced by the increase of the lattice parameters and sintering time

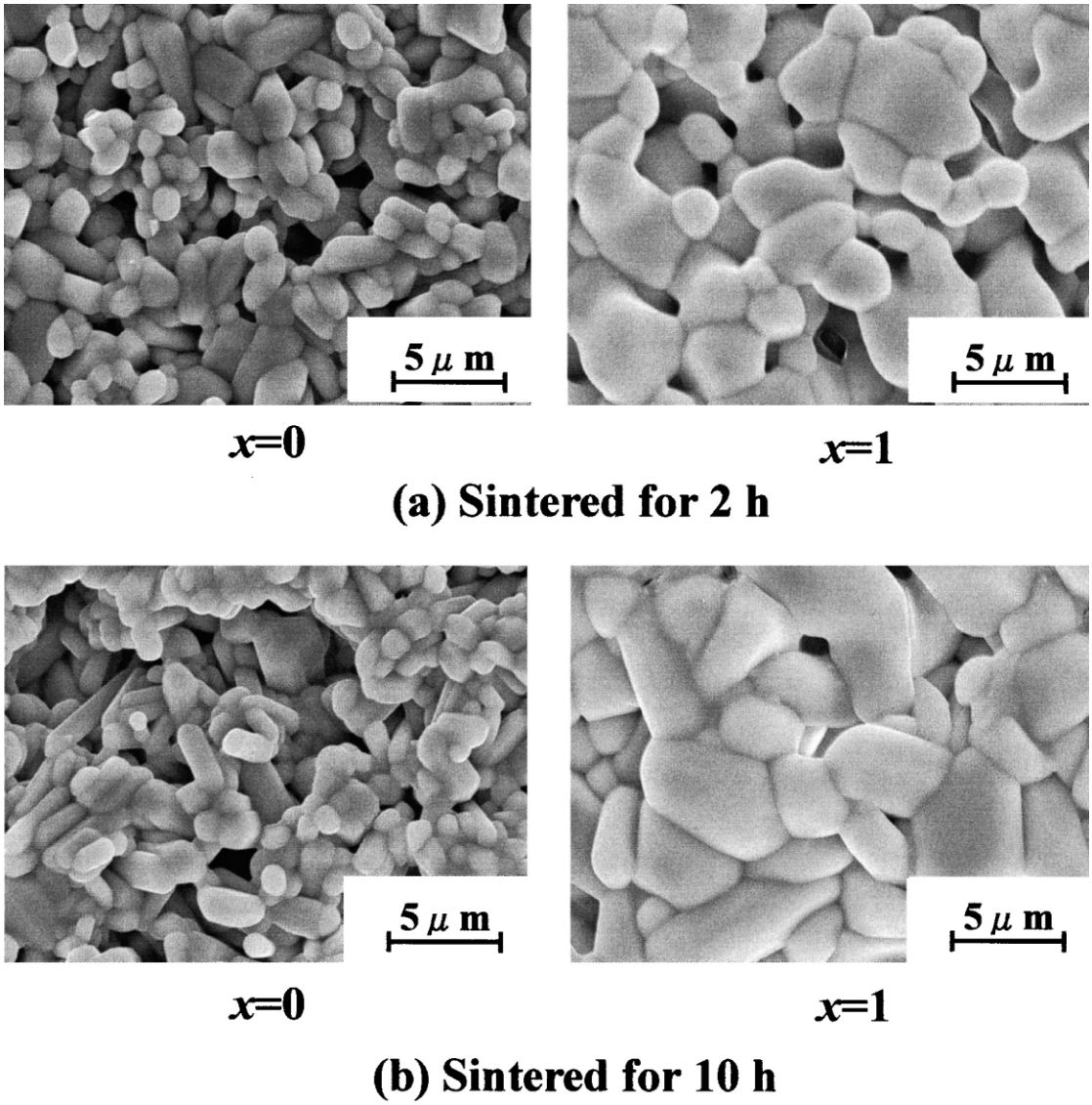

Fig. 3. FE–SEM images of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions without MgO.

are effective in the improvement of the $Q{\cdot}f$ values of this solid solutions.

The microwave dielectric properties of the samples with MgO are also listed in Table 2 and shown in Fig. 2. The ε_r values range from 10.5 to 15.8, and the variations in these values are related to those in the unit cell volumes which is shown in Fig. 1. For this reason, it is considered that the variations in the ε_r values depend on the preferential Mg substitution for Cu. The τ_f values with MgO do not show the significant variations over the whole composition in comparison with these values without MgO. Thus, the MgO doped solid solutions does not influence the variations in the τ_f values over the whole composition as shown in the samples without MgO. However, the $Q{\cdot}f$ values with MgO are increased with increasing the composition, and the highest values is 128333 GHz in $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions ($x=0.25$). Moreover, the $Q{\cdot}f$ values are markedly decreased by increasing the composition over beyond $x=0.25$. These remarkable decreases of the values can be explained in terms of the variation in the microstructures, which is shown in Fig. 4. In the composition range from 0 to 0.25 where Mg^{2+} ions substitute for Cu sites, the grain growth of the solid solutions with MgO was recognized. The improvement of $Q{\cdot}f$ values ($x=0.25$) in comparison with the solid solutions without MgO is attributed to the grain growth by Mg substitution for Cu. On the other hand, in the decreased region of $Q{\cdot}f$ values in which Mg^{2+} ions substitute for Zn sites, the formation of the plate like crystalline of unknown phase including Y, Ba, Zn, O and small amount of Mg is observed as shown in Fig. 4 (b). Also, the particles show Y_2BaZnO_5 compound on the basis of EDX analysis. Thus, it is considered that the formation of the unknown phase occurred by Mg substitution for Zn exerts on the decrease of $Q{\cdot}f$ values and the variations in the microstructure with MgO doping interrelate to the $Q{\cdot}f$ values in this system.

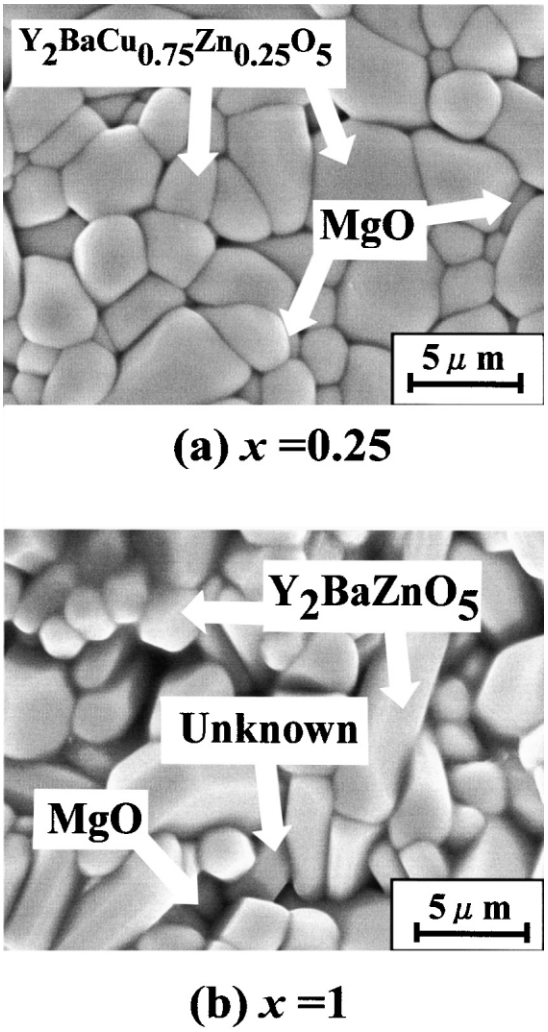

Fig. 4. FE–SEM images of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions with 5 wt.% MgO at (a) $x=0.25$ and (b) $x=1$.

4. Conclusion

The microwave dielectric properties of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions with and without MgO were discussed by evaluating the microstructure and lattice parameters. The lattice parameters on the solid solutions without MgO are closely related to the variations of the atomic distances in the MO_5 pyramid induced by Zn substitution for Cu. Then, the $Q{\cdot}f$ values are linearly increased with increasing the composition, and the highest values of the samples without MgO is 113969 GHz of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ ($x=1$) solid solutions sintered for 10 h. Thus, it is clarified that the $Q{\cdot}f$ values of the solid solutions depend on the variations in the lattice parameters and grain growth induced by increasing in the sintering time. Concerning the microwave dielectric properties and crystal structure with MgO, Mg substitution for Cu and/or Zn takes place depending on the composition, i.e. partial substitution of Cu by Mg at $x=0$ and 0.25 and then the Zn substitutions for Mg at the composition range from 0.5 to 1. Thus, these substitutions influence the variation in the unit cell volumes and ε_r values. Also, it suggests that the microstructure of the MgO doped $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions relate to the improvement of $Q{\cdot}f$ values, and then the highest values is 128333 GHz in the composition $x=0.25$.

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